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5
LAUNDRY DETERGENT COMPOSITIONS COMPRISING A SACCHARIDE
GUM DEGRADING ENZYME

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15
Field of the Invention

The present invention relates to laundry detergent compositions, comprising a saccharide gum degrading enzyme.

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Background of the invention

25 Detergent compositions include nowadays a complex combination of active ingredients which fulfill certain specific needs. In particular, current detergent formulations generally include detergent enzymes providing cleaning and fabric care benefits and more specifically cellulase and amylase enzymes.

30 The efficiency of cellulytic enzymes, i.e. cellulases, in terms of textile cleaning and harshness-reducing agent for fabrics has been recognized for some time. The activity of cellulase is one in which cellulosic fibres or substrates are hydrolysed by the cellulase and depending on the particular function of the cellulase, which can be endo- or exo- cellulase and the respective hemicellulases. The cellulose structures are depolymerized or cleaved into smaller and thereby more soluble or dispersible fractions. This activity in particular on fabrics provides a cleaning, rejuvenation, softening and
35 generally improved handfeel characteristics to the fabric structure.

Amylases are known in the art to provide stain removal performance benefits on naturally present or added starch containing food stains/soils or added as a finishing agent.

5 Food stains/soils represents the majority of consumer relevant stains/soils and often comprise food additives. Neutraceuticals, acidulants, antioxidants, preservatives, sweeteners, enzymes, thickener / stabiliser agents such as hydrocolloids and emulsifiers are commonly used food additives. In particular, the consumer demand for reductions in fat and calories is driving growth in
10 texturing agents as fat replacers. The market for hydrocolloid texturing / stabiliser agent also called food gums, is expected to grow about 4% a year, xanthan gum growth should register gains of 6% to 8%/year and carrageenan about 3%/year (Chemical week, June 19 (1996) pp32-34).

15 The term "gum" denotes a group of industrially useful polysaccharides (long chain polymer) or their derivatives that hydrate in hot or cold water to form viscous solutions, dispersions or gels. Gums are classified as natural and modified. Natural gums include seaweed extracts, plant extrudates, gums from seed or root, and gums obtained by microbial fermentation. Modified
20 (semisynthetic) gums include cellulose and starch derivatives and certain synthetic gums such as low methoxyl pectin, propylene glycol alginate, and carboxymethyl and hydropropyl guar gum (Gums in *Encyclopedia Chemical Technology* 4th Ed. Vol. 12, pp842-862, J. Baird, Kelco division of Merck). See also Carbohydrate Chemistry for Food Scientists (Eagan Press - 1997)
25 by R. L. Whistler and J.N. BeMiller, Chap 4, pp63-89 and Direct Food Additives in Fruit Processing by P. Laslo, Bioprinciples and Applications, Vol1, Chapter II, pp313-325 (1996) Technomic publishing.

30 Some of these gums, such as xanthan gum (E 415, CEE number), gellan gum (E416), guar gum (E412), locust bean (E410) and tragacanth (E413) are widely used alone or in combinations in many food applications (Gums in *ECT* 4th Ed., Vol. 12 pp842-862, J. Baird, Kelco division of Merck). In particular, guar gum is often used in foods as a thickener and a binder of free water in sauces and salad dressings. Guar gum is also used as a binder of free water and
35 stabiliser in ice cream and frozen desserts. Free water in ice cream mix causes a grainy texture, ice crystals, poor meltdown properties and poor heat-shock resistance in the finished ice cream. The incorporation of a stabiliser containing

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guar gum in quantities up to about 0.3% of the ice cream mix yields a smooth-textured, chewy product with slow-melting down properties and good heat shock resistance. It is also particularly suitable for flash pasteurisation because of its rapid hydration properties. Other foods that can be stabilised with guar gum because of its ability to bind water, are frozen foods, cheeses, pie fillings, icings and pet foods. Other examples include : algin gums are known to be used in sherbet, canned and fabricated food, tragacanth gums used in salad dressings, xanthan for dairy products and beverages. Gellans are found in icing, frosting and dairy products and locust bean and agar in ice creams.

The specificity of these food gums is that they give a high to very high viscosity solution when hydrated in water. Some of these gums such as guar, algin, arabic, karaya, methyl cellulose locust bean gums are also used in the paper industry and chosen for their high affinity for cellulosic fibres (Industrial gums by R. L. Whistler and J.N. BeMiller (Academic Press - 1973). Their potential to flocculate clays and other inorganic materials such as calcium salts, are used in other applications such as water treatment. The high viscosity of these food gums is desirable for all the above mentioned food and other applications.

However, it has been surprisingly found that these food gums adsorb strongly onto the cotton fibers of the fabric, thereby gluing the stains/soils on the fabric. Even when the gum is present at a very low level in the food compositions, such as 0.01% to 5%, more usually between 0.01% to 0.8%.

It has been also surprisingly found that the capability of these food gums to flocculate clays results in the dinginess and yellowing of the fabric. This is particularly important since, the overall performance of a detergent is judged by not only its ability to remove soils and stains but also its ability to prevent redeposition of the soils, or the breakdown products of the soils or of any insoluble salt, on the article washed. Redeposition effects results in the articles being coated in an unseemly film, appearing streaked or being covered in visible spots which remain intact at the end of the wash process. These residues build up on the fabric leading to dinginess and yellowing.

As can be seen from the above, there is a continuous need to formulate laundry detergent compositions which provide excellent overall cleaning

performance. Accordingly it is an object of the present invention to provide a laundry detergent composition which delivers superior cleaning and whiteness performance benefits, especially excellent food stain/soil removal, dingy cleaning and whiteness maintenance.

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The above objective has been met by formulating laundry detergent compositions comprising a saccharide gum degrading enzyme.

10 It has been surprisingly found that the laundry detergent composition of the present invention comprising a saccharide gum degrading enzyme, provides excellent food stain/soil removal, dingy cleaning and whiteness maintenance resulting from the hydrolysis of the food saccharide gums binding food or clays stains/soils to cotton fabrics. It has been further found that the performance of the laundry detergent compositions of the present invention is
15 enhanced by the addition of selected surfactants, another enzyme, a builder and/or a bleach system.

20 GB2-169-393 describes a method for removing cellulose contaminant and other vegetable contaminants from fabrics, using the conventional machinery and equipment of dye-house and finishing mills by treatment with an enzymatic preparation containing cellulolytic and pectinolytic enzymes that allow for a reduction of H_2SO_4 concentration below 2% during fabric carbonisation.

25 WO96/06532 relates to a composition capable of killing or inhibiting growing microbial cells by means of a basic protein or peptide of biological origin, e.g. protamine or protamine sulphate. For certain bacteria or fungi, these composition further comprise an oxidoreductase or cell-wall degrading enzyme such as an endoglycosidase type II, a lysozyme and/or a chitinase.

30

WO95/35362 describes to cleaning compositions, including laundry, dishwashing and especially household cleaning compositions, comprising cell wall degrading enzymes having pectinases and/or hemicellulases and optionally cellulases. These compositions are particularly suitable for removing
35 stains of vegetable origin and soil and dirt having a similar structure. These plant cell wall degrading enzymes degrade the structural components of the plant cell walls such as the structured polysaccharides (cellulose,

hemicellulose, pectins) and encompass cellulolytic, pectin degrading and hemicellulose degrading enzymes. A large number of plant cell wall degrading enzyme exist. Cellulolytic enzymes have divided into three classes : endoglucanases, exoglucanases or cellobiohydrolases and β -glucosidases. A large number of enzymes are known to degrade pectins; examples are pectin esterase, pectin lyase, pectate lyase, and endo- or exo-polygalacturonase. In addition to these enzymes degrading the smooth regions, enzymes degrading hairy regions such as rhamnogalacturonase and accessory enzymes have also been found. A multitude of enzymes is available to degrade the hemicellulose structures such as xylanase, galactanase, arabinase, lichenase and mannanase.

However, the use of saccharide gum degrading enzymes for excellent cleaning performance on cotton fabrics in laundry detergent compositions, has never been previously recognised.

Summary of the invention

The present invention relates to laundry detergent compositions comprising a saccharide gum degrading enzyme, providing excellent cleaning performance on cotton fibers, especially food stain/soil removal, dingy cleaning and whiteness maintenance benefits.

Detailed description of the invention

An essential component of the laundry detergent compositions of the present invention is a saccharide gum degrading enzyme. These enzymes are able to hydrolyse non starch, non cellulose, food polysaccharides having a viscosity higher than 800 cps at 1% solution (Measured in water at 25°C, Brookfield Synchro-Lectric viscosimeter at 20 rpm).

It has been surprisingly found that the laundry detergent compositions of the present invention provide excellent cleaning and whiteness performance and especially significant food stain/soil removal benefits and dingy stain/soil cleaning.

Without wishing to be bound by theory, it is believed that saccharide gum degrading enzymes hydrolyse the food gums additives present in food stains/soils, that glue the stains/soils to the cotton fibres. Indeed, it has been found that these non starch, non cellulose food polysaccharides have a high affinity for the cotton fibres thereby binding the stains/soils to the fabric. The hydrolysis of these non starch, non cellulose food polysaccharides release therefore the stains/soils from the cotton textile.

Moreover, it has been surprisingly found that the laundry detergent composition of the present invention provide significant dingy cleaning and whiteness maintenance. Without wishing to be bound by theory, it is believed that the saccharides, being breakdown products of the partial cleaning of these food stains/soils by current detergent formulations, redeposit on the fabric and react with particulate soils such as clay compounds, leading to the dinginess of the cotton fabric. The saccharide gum degrading enzymes of the present invention, hydrolyse the film of saccharides deposited onto the fabrics, thereby preventing the flocculation of these compounds with particulate soils.

Without wishing to be bound by theory, it is also believed that the enzymatic action of the saccharide gum degrading enzymes of the present invention renders the food and dingy stains/soils more accessible to the other detergent components of the laundry detergent composition. Especially, it has been found that the performance of the laundry detergent composition of the present invention is enhanced by the combination with a selected surfactant, another enzyme, a builder and/or a bleach system.

The enzymes of the present invention have a main or side activity on the non starch, non cellulose, food polysaccharides having a viscosity higher than 800cps at 1% solution, such as agar, algin, karawa, tragacanth, guar gum, locus beam, xathan and/or mixtures thereof.

Examples of the industrial gums used separately or in combination as food additives are :

- Seed Gums such as Guar Gum, Locust Bean Quince seed Psyllium, Flax seed and Okra Gums, Tamarin, Larch Arabinogalactan;
- Plant exudates such as Arabic, Ghatti, Karaya, Tragacanth;

- Seaweed extracts such as Algin, Agar, Carrageenan, Fucoidan, Furcellaran, and - Biosynthetic gums such as Xanthan.

Suitable enzymes for the purpose of the present invention have the following
5 main or side enzymatic activity :

- Arabinases : Endo Arabinase (E.C. 3.2.1.99), such as endo α -1,5-arabinosidase, exo Arabinase (E.C. 3.2.1.55), exo A (α -1,2; α -1,3) arabinofuranosidase, exo B (α -1,3; α -1,5) arabinofuranosidase;
- (α -1,2; α -1,3) fucosidase, α -1,6-fucosidase (E.C. 3.2.1.127);
- 10 - β -1,2-Galactanase, β -1,3-Galactanase (E.C. 3.2.1.90), β -1,4-Galactanase, β -1,6-Galactanase, Galactanase are also called Arabino galactan galactosidase (E.C. 3.2.1.89), α and β galactosidase (E.C. 3.2.1.22 & 23), (E.C. 3.2.1.102) (E.C. 3.2.1.103)
- β -Mannosidase (3.2.1.25), α -Mannosidase (3.2.1.24), β -1,2-Mannosidase, α
- 15 -1,2-Mannosidase (E.C. 3.2.1.113) (E.C. 3.2.1.130), α -1,2-1.6 -Mannosidase (3.2.1.137), β -1,3-Mannosidase (E.C. 3.2.1.77), β -1,4-Mannosidase (E.C. 3.2.1.78), β -1,6-Mannosidase (E.C. 3.2.1.101), α -1,3-1,6-Mannosidase (E.C. 3.2.1.114), β -1,4-Mannobiosidase (E.C. 3.2.1.100), Mannosidase are also called mannanase or mannase,
- 20 - Glucuronosidase (E.C. 3.2.1.131), glucuronidase (E.C. 3.2.1.31). exo 1,2 or 1,4 glucuronidase,
- Agarase (E.C. 3.2.1.81), Carrageenase (E.C. 3.2.1.83), α -1,2-, Xanthan lyase; Poly(α -L guluronate) lyase , also called Alginase II (E.C. 4.2.2.11)
- 25 Preferred saccharide gums degrading enzymes are :
- Mannosidase : β -mannosidase, endo 1,4- β -D mannosidase, endo 1,2- β -D mannosidase, and exo 1,3- β -D mannosidase;
- Galactosidase : exo 1,6- β -D-galactosidase and 1,3- β -D-galactosidase;
- Glucuronidase, glucuronosidase and exo 1,2 or 1,4 glucuronidase;
- 30 - Arabinase : endo α -1,5-arabinosidase, exo Arabinase, exo A (α -1,2; α -1,3) arabinofuranosidase, exo B (α -1,3; α -1,5) arabinofuranosidase;
- Xanthan lyase; Poly(α -L guluronate) lyase; Agarase, and Carrageenase.

In particular the following enzymes are preferred saccharide gum
35 degrading enzymes for specific non starch, non cellulose, food polysaccharide having a viscosity higher than 800 cps at 1% solution. Enzymes hydrolysing guar and locust bean gums are mannosidase, galactomannosidase

preferentially endo mannosidase and galactomannosidase enzyme such as Gamanase[®] being a galactomannanase from *Aspergillus niger*. Preferred enzymes for degrading xanthan gums are mannosidase, glucuronosidase and glucosidase. Preferred enzymes are galactosidase, rhamnogalacturonase to
5 degrade Karaya gum. Preferred enzymes are galacturonase, galactosidase, fucosidase, arabanase to degrade Tragacanth gums. Preferred enzymes for degrading gellan, agar and carrageenan gums are respectively, glucosidase, rhamnosidase and glucuronidase; agarase and carrageenase. Preferred
10 enzymes are mannuronase and guluronase that degrade the mannopyranosyluronic and gulopyranosyluronic moiety contained in alginate.

Arabin-degrading enzymes are known to be produced by a variety of plants and micro-organisms. Three enzymes obtainable from *A. niger* have been cloned by molecular biological techniques (EP-A-506,190). Also
15 arabinosidase from bacteria such as *Bacteroides* has been cloned (Whitehead and Hesoell (1990) J. Bacteriol. 172, 2408). An enzyme exhibiting arabinase activity derived from *Aspergillus aculeatus* useful for degrading plant cell wall components has been described in Novo Nordisk A/S WO94/24269.

20 New rhamnogalacturonase enzyme derived from *Aspergillus aculeatus* in Novo Nordisk A/S WO94/20612; a rhamnogalacturonase having specific partial aminoacid sequence, obtained from *Aspergillus aculeatus*, *A. Japonicus* or *Irpex lactis* in Novo Nordisk A/S WO92/19728 and a new recombinant DNA encoding rhamnogalacturonase in Unilever EP 570 075 have been described
25 for degrading plant cell wall components. WO93/20190 describes rhamnogalacturonan acetyl esterase enzyme obtained from *Aspergillus aculeatus* to degrade acetylated modified hairy regions of vegetable material.

Mannanases enzymes are described in PCT application WO93/24662
30 which discloses mannase enzymes, their coding genes, their isolation methods and methods for bleaching lignocellulosic pulps. New β -1,4-galactanase from *Aspergillus aculeatus* is disclosed in EP 498 137 for degrading or modifying plant cell walls.

35 Commercially available saccharide gum degrading enzymes are the galactomannanase sold under the tradename Gammanase[®] and the arabanase sold under the trade name Pectinex AR by Novo Nordisk A/S. Also

are the enzymes sold under the tradenames the Pectinex Ultra SP by Novo Nordisk A/S, Rapidase Pineapple by Gist -Brocades, Rohapec B1L by Rohm; all enzymatic preparations having a galactomannanase, arabinogalactanase, galactoglucomannanase and/or arabinoxylanase activity. The galactomannanase
5 can be extracted from the commercial Rohapec B1L sample using the following protocol (Method In Enzymology, Guide to Protein Purification Vol 182, ISBN 012 18 20 831) with a buffer: 50 mM methyl-piperazine, 50 mM Bis-Tris, 25 mM Tris, adjusted at pH 8 with HCl and the anion exchange chromatography with the chromatography support Q-Hyper D (0.5 x 10 cm) (Biosepra) and the
10 elution solution being Sodium Chloride linear gradient (0 - 0.5 M) at a flow rate of 10 ml/min. Also available is the saccharide gum degrading enzyme sold under the tradename Rapidase light by Gist-Brocades and endo-galactanase form Megazyme Ltd (Australia).

15 This saccharide gum degrading enzyme is incorporated into the compositions in accordance with the invention preferably at a level of from 0.0001% to 2%, more preferably from 0.0005% to 0.1%, most preferred from 0.0006% to 0.015% pure enzyme by weight of the composition.

20 Preferred saccharide gum degrading enzymes for specific applications are alkaline saccharide gum degrading enzymes, ie enzymes having an enzymatic activity of at least 10%, preferably at least 25%, more preferably at least 40% of its maximum activity at a pH ranging from 7 to 12. More preferred are enzymes having their maximum activity at a pH ranging from 7 to 12.

25 The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified
30 forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein-/ genetic engineering techniques in order to optimise their performance efficiency in the cleaning compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such
35 compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified
5 by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing metal binding sites to increase chelant stability.

10 Detergent components

The laundry detergent compositions of the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical
15 form of the composition, and the nature of the cleaning operation for which it is to be used.

The laundry detergent compositions of the present invention preferably further comprise a detergent ingredient selected from a selected surfactant,
20 another enzyme, a builder and/or a bleach system.

The laundry detergent compositions according to the invention can be liquid, paste, gels, bars, tablets, spray, foam, powder or granular forms. Granular compositions can also be in "compact" form, the liquid compositions
25 can also be in a "concentrated" form.

One preferred type of gel detergent is a heavy duty gel laundry detergent composition comprising from 15% to 40% by weight of an anionic surfactant component which comprises : (i) from 5% to 25% by weight of alkyl
30 polyethoxylate sulfates wherein the alkyl group contains from about 10 to about 22 carbon atoms and the polyethoxylate chain contains from 0.5 to about 15, preferably from 0.5 to about 5, more preferably from 0.5 to about 4, ethylene oxide moieties; and (ii) from 5% to 20% by weight of fatty acids.

Gel compositions herein may further contain one or more additional
35 deterative additives selected from the group consisting of non-citrate builders, optical brighteners, soil release polymers, dye transfer inhibitors, polymeric dispersing agents, enzymes, suds suppressers, dyes, perfumes, colorants, filler

salts, hydrotropes, antiredeposition agents, antifading agent, dye fixative agents, prill/fuzzing reducing agents, and mixtures thereof.

The gel compositions herein have a viscosity at 20 s^{-1} shear rate of from about 100 cp to about 4,000 cp, preferably from about 300 cp to about 3,000 cp, more preferably from about 500 cp to about 2,000 cp and are stable upon storage.

Without being limited by theory, it is believed that the presence of electrolytes acts to control the viscosity of the gel compositions. Thus, the gel nature of the compositions herein are affected by the choice of surfactants and by the amount of electrolytes present. In preferred embodiments herein, the compositions will further comprise from 0% to about 10%, more preferably from about 2% to about 6%, even more preferably from about 3% to about 5%, of a suitable electrolyte or acid equivalent thereof. Sodium citrate is a highly preferred electrolyte for use herein.

The compositions herein may optionally contain from about 0% to about 10%, by weight, of solvents and hydrotropes. Without being limited by theory, it is believed that the presence of solvents and hydrotropes can affect the structured versus isotropic nature of the compositions; By "solvent" is meant the commonly used solvents in the detergent industry, including alkyl monoalcohol, di-, and tri-alcohols, ethylene glycol, propylene glycol, propanediol, ethanediol, glycerine, etc. By "hydrotrope" is meant the commonly used hydrotropes in the detergent industry, including short chain surfactants that help solubilize other surfactants. Other examples of hydrotropes include cumene, xylene, or toluene sulfonate, urea, C_8 or shorter chain alkyl carboxylates, and C_8 or shorter chain alkyl sulfate and ethoxylated sulfates.

Fatty acids of use herein include saturated and/or unsaturated fatty acids obtained from natural sources or synthetically prepared. Examples of fatty acids include capric, lauric, myristic, palmitic, stearic, arachidic, and behenic acid. Other fatty acids include palmitoleic, oleic, linoleic, linolenic, and ricinoleic acid.

The compositions of the invention may be formulated hand and machine laundry detergent compositions including laundry additive compositions and compositions suitable for use in the soaking and/or pretreatment of stained fabrics, rinse added fabric softener compositions.

When formulated as compositions suitable for use in a laundry machine washing method, the compositions of the invention preferably contain both a surfactant and a builder compound and additionally one or more detergent components preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors. Laundry compositions can also contain softening agents, as additional detergent components. Such compositions containing an enzyme hydrolysing saccharides gums, can provide fabric cleaning, stain removal, whiteness maintenance, softening, colour appearance and dye transfer inhibition.

The compositions of the invention can also be used as detergent additive products. Such additive products are intended to supplement or boost the performance of conventional detergent compositions.

If needed the density of the laundry detergent compositions herein ranges from 400 to 1200 g/litre, preferably 500 to 950 g/litre of composition measured at 20°C.

The "compact" form of the compositions herein is best reflected by density and, in terms of composition, by the amount of inorganic filler salt; inorganic filler salts are conventional ingredients of detergent compositions in powder form; in conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% by weight of the total composition. In the compact compositions, the filler salt is present in amounts not exceeding 15% of the total composition, preferably not exceeding 10%, most preferably not exceeding 5% by weight of the composition. The inorganic filler salts, such as meant in the present compositions are selected from the alkali and alkaline-earth-metal salts of sulphates and chlorides. A preferred filler salt is sodium sulphate.

Liquid detergent compositions according to the present invention can also be in a "concentrated form", in such case, the liquid detergent compositions according the present invention will contain a lower amount of water, compared to conventional liquid detergents. Typically the water content of the concentrated liquid detergent is preferably less than 40%, more

preferably less than 30%, most preferably less than 20% by weight of the detergent composition.

Surfactant system

5

The laundry detergent compositions according to the present invention generally comprise a surfactant system wherein the surfactant can be selected from nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants. Preferably, the laundry detergent compositions of the present invention will comprise a nonionic, an anionic and/or a cationic surfactant.

It has been surprisingly found that the laundry detergent composition of the present invention further comprising a nonionic, an anionic surfactant and/or a cationic surfactant, provide enhanced food stain/soil removal, dingy cleaning and whiteness maintenance.

Without wishing to be bound by theory, it is believed that the enzymatic hydrolysis results in small particles being more easily removed by nonionic surfactants known to focus on particulate soiling. Preferred nonionic surfactants are alkyl ethoxylate AE3 to AE7. It is also believed that the combination of the fabric substantive cationic surfactant with the enzymatic hydrolysis of the saccharide gums degrading enzyme provides improved performances.

The surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation are 1% to 35% by weight, most preferably from 1% to 30% by weight of laundry detergent compositions in accord with the invention.

The surfactant is preferably formulated to be compatible with enzyme components present in the composition. In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of any enzyme in these compositions.

Nonionic surfactants

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates

being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include IgepalTM CO-630, marketed by the GAF Corporation; and TritonTM X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type include TergitolTM 15-S-9 (the condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide), TergitolTM 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; NeodolTM 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), NeodolTM 23-3 (the condensation product of C₁₂-C₁₃ linear alcohol with 3.0 moles of ethylene oxide), NeodolTM 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), NeodolTM 45-5 (the condensation product of C₁₄-C₁₅ linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, KyroTM EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O3O or O5O (the condensation product of C₁₂-C₁₄

alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

The preferred alkylpolyglycosides have the formula:



wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

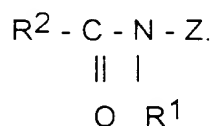
The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a

molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available PlurafacTM LF404 and PluronicTM surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C₈-C₁₄ alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C₈-C₁₈ alcohol ethoxylates (preferably C₁₀ avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula:



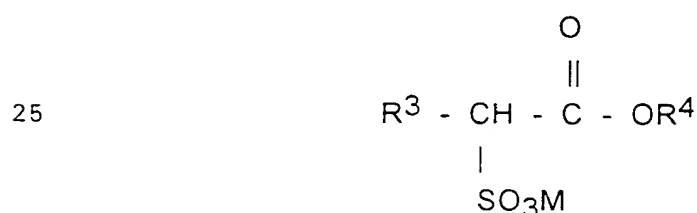
wherein R^1 is H, or R^1 is C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof.

- 5 Preferably, R^1 is methyl, R^2 is a straight C_{11-15} alkyl or C_{16-18} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

10 *Anionic surfactants*

Preferred anionic surfactants for the purpose of the present invention are alkyl esters sulfates and linear alkyl benzene surfactants. Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C_8-C_{20} carboxylic acids (i.e., fatty acids) 15 which are sulfonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry 20 applications, comprise alkyl ester sulfonate surfactants of the structural formula:



wherein R^3 is a C_8-C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a C_1-C_6 hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R^3 is 30 $C_{10}-C_{16}$ alkyl, and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R^3 is $C_{10}-C_{16}$ alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula ROSO_3M wherein R preferably is a C_{10} - C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10} - C_{20} alkyl component, more preferably a C_{12} - C_{18} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C_{12} - C_{16} are preferred for lower wash temperatures (e.g. below about 50°C) and C_{16} - C_{18} alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for deterative purposes can also be included in the laundry detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_8 - C_{22} primary or secondary alkanesulfonates, C_8 - C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C_8 - C_{24} alkylpolyglycoethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C_{12} - C_{18} monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C_6 - C_{12} diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_k\text{CH}_2\text{COO-M}^+$ wherein R is a C_8 - C_{22} alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

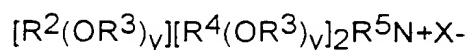
Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.

Highly preferred anionic surfactants include alkyl alkoxyated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C_{10} - C_{24} alkyl or hydroxyalkyl group having a C_{10} - C_{24} alkyl component, preferably a C_{12} - C_{20} alkyl or hydroxyalkyl, more preferably C_{12} - C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12} - C_{18} alkyl polyethoxylate (1.0) sulfate (C_{12} - $C_{18}E(1.0)M$), C_{12} - C_{18} alkyl polyethoxylate (2.25) sulfate (C_{12} - $C_{18}E(2.25)M$), C_{12} - C_{18} alkyl polyethoxylate (3.0) sulfate (C_{12} - $C_{18}E(3.0)M$), and C_{12} - C_{18} alkyl polyethoxylate (4.0) sulfate (C_{12} - $C_{18}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

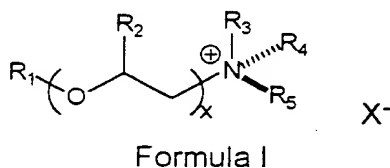
30 *Cationic surfactants*

Cationic deterative surfactants suitable for use in the laundry detergent compositions of the present invention are those having one long-chain hydrocarbly group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula :

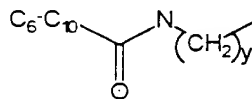


wherein R^2 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2OH)-$, $-CH_2CH_2CH_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups, $-CH_2CHOH-CHOHCOR^6CHOHCH_2OH$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Quaternary ammonium surfactant suitable for the present invention has the formula (I):



whereby R^1 is a short chainlength alkyl (C₆-C₁₀) or alkylamidoalkyl of the formula (II):



25

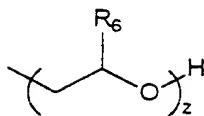
y is 2-4, preferably 3.

whereby R^2 is H or a C₁-C₃ alkyl,

whereby x is 0-4, preferably 0-2, most preferably 0,

whereby R^3 , R^4 and R^5 are either the same or different and can be either a short chain alkyl (C₁-C₃) or alkoxylated alkyl of the formula III,

whereby X^- is a counterion, preferably a halide, e.g. chloride or methylsulfate.



Formula III

- 5 R₆ is C₁-C₄ and z is 1 or 2.

Preferred quat ammonium surfactants are those as defined in formula I whereby

R₁ is C₈, C₁₀ or mixtures thereof, x=0,

- 10 R₃, R₄ = CH₃ and R₅ = CH₂CH₂OH.

Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :

- 15 $R_1R_2R_3R_4N^+X^-$ (i)

wherein R₁ is C₈-C₁₆ alkyl, each of R₂, R₃ and R₄ is independently C₁-C₄ alkyl, C₁-C₄ hydroxy alkyl, benzyl, and -(C₂H₄)_xH where x has a value from 2 to 5, and X is an anion. Not more than one of R₂, R₃ or R₄ should be benzyl.

- 20 The preferred alkyl chain length for R₁ is C₁₂-C₁₅ particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R₂R₃ and R₄ are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

- 25 Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

- coconut trimethyl ammonium chloride or bromide;
 coconut methyl dihydroxyethyl ammonium chloride or bromide;
 decyl triethyl ammonium chloride;
 30 decyl dimethyl hydroxyethyl ammonium chloride or bromide;
 C₁₂-15 dimethyl hydroxyethyl ammonium chloride or bromide;
 coconut dimethyl hydroxyethyl ammonium chloride or bromide;
 myristyl trimethyl ammonium methyl sulphate;
 lauryl dimethyl benzyl ammonium chloride or bromide;
 35 lauryl dimethyl (ethenoxy)₄ ammonium chloride or bromide;

choline esters (compounds of formula (i) wherein R_1 is $CH_2-CH_2-O-C-C_{12-14}$ alkyl and $R_2R_3R_4$ are methyl).



5 di-alkyl imidazolines [compounds of formula (i)].

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

10

Typical cationic fabric softening components include the water-insoluble quaternary-ammonium fabric softening actives or their corresponding amine precursor, the most commonly used having been di-long alkyl chain ammonium chloride or methyl sulfate.

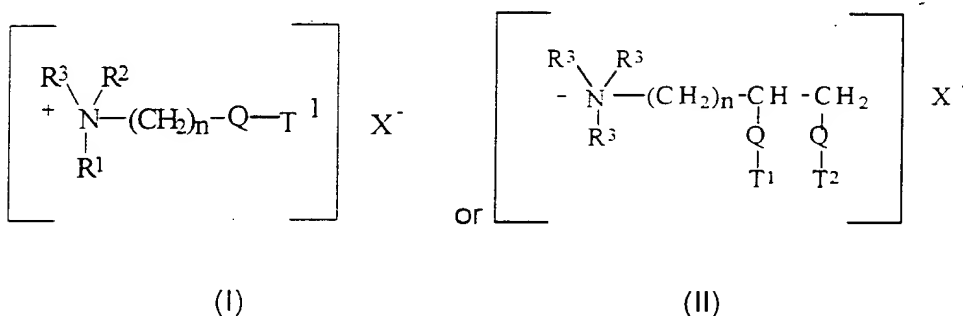
15 Preferred cationic softeners among these include the following:

- 1) ditallow dimethylammonium chloride (DTDMAC);
- 2) dihydrogenated tallow dimethylammonium chloride;
- 3) dihydrogenated tallow dimethylammonium methylsulfate;
- 4) distearyl dimethylammonium chloride;
- 20 5) dioleyl dimethylammonium chloride;
- 6) dipalmityl hydroxyethyl methylammonium chloride;
- 7) stearyl benzyl dimethylammonium chloride;
- 8) tallow trimethylammonium chloride;
- 9) hydrogenated tallow trimethylammonium chloride;
- 25 10) C_{12-14} alkyl hydroxyethyl dimethylammonium chloride;
- 11) C_{12-18} alkyl dihydroxyethyl methylammonium chloride;
- 12) di(stearoyloxyethyl) dimethylammonium chloride (DSOEDMAC);
- 13) di(tallow-oxy-ethyl) dimethylammonium chloride;
- 14) ditallow imidazolinium methylsulfate;
- 30 15) 1-(2-tallowylamidoethyl)-2-tallowyl imidazolinium methylsulfate.

Biodegradable quaternary ammonium compounds have been presented as alternatives to the traditionally used di-long alkyl chain ammonium chlorides and methyl sulfates. Such quaternary ammonium compounds contain long
35 chain alk(en)yl groups interrupted by functional groups such as carboxy groups. Said materials and fabric softening compositions containing them are

disclosed in numerous publications such as EP-A-0,040,562, and EP-A-0,239,910.

The quaternary ammonium compounds and amine precursors herein have the
5 formula (I) or (II), below :



10

wherein Q is selected from -O-C(O)-, -C(O)-O-, -O-C(O)-O-, -NR⁴-C(O)-, -C(O)-NR⁴-;

R¹ is (CH₂)_n-Q-T² or T³;

R² is (CH₂)_m-Q-T⁴ or T⁵ or R³;

15

R³ is C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl or H;

R⁴ is H or C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl;

T¹, T², T³, T⁴, T⁵ are independently C₁₁-C₂₂ alkyl or alkenyl;

n and m are integers from 1 to 4; and

20

X⁻ is a softener-compatible anion. Non-limiting examples of softener-compatible anions include chloride or methyl sulfate.

25

The alkyl, or alkenyl, chain T¹, T², T³, T⁴, T⁵ must contain at least 11 carbon atoms, preferably at least 16 carbon atoms. The chain may be straight or branched. Tallow is a convenient and inexpensive source of long chain alkyl and alkenyl material. The compounds wherein T¹, T², T³, T⁴, T⁵ represents the mixture of long chain materials typical for tallow are particularly preferred.

Specific examples of quaternary ammonium compounds suitable for use in the aqueous fabric softening compositions herein include :

- 30
- 1) N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
 - 2) N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;
 - 3) N,N-di(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;

- 4) N,N-di(2-tallowyl-oxy-ethylcarbonyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
- 5) N-(2-tallowyl-oxy-2-ethyl)-N-(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 6) N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
- 7) N-(2-tallowyl-oxy-2-oxo-ethyl)-N-(tallowyl-N,N-dimethyl-ammonium chloride; and
- 8) 1,2-ditallowyl-oxy-3-trimethylammoniopropane chloride;
- and mixtures of any of the above materials.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

Conventional detergent enzymes

The laundry detergent compositions will preferably comprise in addition to the saccharide gum degrading enzyme one or more enzymes which provide cleaning performance, fabric care and/or sanitisation benefits, preferably a cellulase, and/or amylase.

It has been surprisingly found that the laundry detergent compositions of the present invention further comprising another enzyme, especially a cellulase and/or an amylase provide enhanced food stain/soil removal, dingy cleaning and whiteness maintenance. In particular, it has been found that cellulolytic enzymes are particularly useful in degrading cellulose polysaccharide food additives and thereby useful in helping the cleaning of food stain/soil from cotton fabrics.

Without wishing to be bound by theory, it is believed that this improved performance is resulting from the combined enzymatic hydrolysis's of the cellulase enzyme on the cotton fabric support and of the saccharide gum degrading enzyme on the polysaccharide binding the stain onto the cotton fabric support. Similarly, the combined action of the amylase on the starch-based finishing agent covering the surface of the cotton fabric and of the saccharide gum degrading enzyme on the polysaccharide binding the stain onto the cotton fabric, gives enhanced performance.

Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, 5 oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, β -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof.

The cellulases usable in the present invention include both bacterial or 10 fungal cellulases. Preferably, they will have a pH optimum of between 5 and 12 and a specific activity above 50 CEVU/mg (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, J61078384 and WO96/02653 which discloses fungal cellulase produced respectively from *Humicola insolens*, *Trichoderma*, *Thielavia* and *Sporotrichum*. 15 EP 739 982 describes cellulases isolated from novel *Bacillus* species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO95/26398.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* 20 strain DSM 1800.

Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from *Humicola insolens*, DSM 1800, exhibiting cellulase activity; a preferred 25 endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from *Trichoderma longibrachiatum* described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are 30 cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and WO91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 and WO95/24471.

35 Said cellulases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Amylases (α and/or β) can be included for removal of carbohydrate-based stains. WO94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also
5 WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in cleaning compositions include both α - and β -amylases. α -Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo).
10 Other suitable amylases are stability-enhanced amylases described in WO94/18314, published August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases
15 described in EP 277 216, WO95/26397 and WO96/23873 (all by Novo Nordisk).

Examples of commercial α -amylases products are Purafect Ox Am[®] from Genencor and Termamyl[®], Ban[®], Fungamyl[®] and Duramyl[®], all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable
20 amylases : α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl[®] at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas[®] α -amylase activity assay. Suitable are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Other amylolytic enzymes with
25 improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The amylolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme
30 by weight of the composition.

A preferred combination is a laundry detergent composition having cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase in conjunction with one or more plant cell wall
35 degrading enzymes.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc and with a phenolic substrate as bleach enhancing molecule. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Enhancers are generally comprised at a level of from 0.1% to 5% by weight of total composition. Preferred enhancers are substituted phenothiazine and phenoxazine 10-Phenothiazinepropionic acid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substituted syringates (C3-C5 substituted alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1

Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R(Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitable are the lipolytic enzymes described in EP 258 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor); WO 90/09446 (Plant Genetic System) and WO 94/14963 and WO 94/14964 (Unilever).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE[®] by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE[®], DURAZYM[®] and SAVINASE[®] from Novo and MAXATASE[®], MAXACAL[®], PROPERASE[®] and MAXAPEM[®] (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein. Suitable is the protease called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived

from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994. Also suitable is a carbonyl hydrolase variant of the protease described in WO95/10591, having an amino acid sequence derived by replacement of a plurality of amino acid residues replaced in the precursor enzyme corresponding to position +210 in combination with one or more of the following residues : +33, +62, +67, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218, and +222, where the numbered position corresponds to naturally-occurring subtilisin from *Bacillus amyloliquefaciens* or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins, such as *Bacillus lentus* subtilisin (co-pending patent application US Serial No. 60/048,550, filed June 04, 1997).

Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221.

See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

The proteolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimise their performance efficiency in the cleaning compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability. Special attention must be paid to the cellulases as most of the cellulases have separate binding domains (CBD). Properties of such enzymes can be altered by modifications in these domains.

Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc... containing one enzyme) or as mixtures of two or more enzymes (e.g. cogramulates).

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO

9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Bleaching agent

15

It has been surprisingly found that the laundry detergent composition of the present invention further comprising a bleaching agent, especially a bleach activator bleaching system, provide enhanced food stain/soil removal, dingy cleaning and whiteness maintenance. Without wishing to be bound by theory, it is believed that the smaller chromophoric particles resulting from the saccharide gums degrading enzyme hydrolysis are more easily attacked by the bleach activated bleaching systems, especially at low temperature.

Additional optional detergent ingredients that can be included in the laundry detergent compositions of the present invention include bleaching agents such as hydrogen peroxide, PB1, PB4 and percarbonate with a particle size of 400-800 microns.

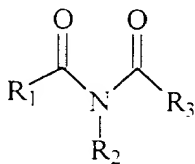
These bleaching agent components can include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators. When present oxygen bleaching compounds will typically be present at levels of from about 1% to about 25%.

The bleaching agent component for use herein can be any of the bleaching agents useful for laundry detergent compositions including oxygen bleaches as well as others known in the art. The bleaching agent suitable for the present invention can be an activated or non-activated bleaching agent.

One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Application 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551.

Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetythylenediamine (TAED), nonanoyloxybenzene-sulfonate (NOBS, described in US 4,412,934), 3,5-trimethylhexanoloxybenzenesulfonate (ISONOBS, described in EP 120,591) or pentaacetylglucose (PAG) or Phenolsulfonate ester of N-nonanoyl-6-aminocaproic acid (NACA-OBS, described in WO94/28106), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect. Also suitable activators are acylated citrate esters such as disclosed in Copending European Patent Application No. 91870207.7 and unsymmetrical acyclic imide bleach activator of the following formula as disclosed in the Procter & Gamble co-pending patent applications US serial No. 60/022,786 (filed July 30, 1996) and No. 60/028,122 (filed October 15, 1996) :



wherein R₁ is a C₇-C₁₃ linear or branched chain saturated or unsaturated alkyl group, R₂ is a C₁-C₈, linear or branched chain saturated or unsaturated alkyl

group and R₃ is a C₁-C₄ linear or branched chain saturated or unsaturated alkyl group.

5 Useful bleaching agents, including peroxyacids and bleaching systems comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention are described in our co-

pending applications USSN 08/136,626, PCT/US95/07823, WO95/27772, WO95/27773, WO95/27774 and WO95/27775.

10 The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

15 Metal-containing catalysts for use in bleach compositions, include cobalt-containing catalysts such as Pentaamine acetate cobalt(III) salts and manganese-containing catalysts such as those described in EPA 549 271; EPA 549 272; EPA 458 397; US 5,246,621; EPA 458 398; US 5,194,416 and US

20 5,114,611. Bleaching composition comprising a peroxy compound, a manganese-containing bleach catalyst and a chelating agent is described in the patent application No 94870206.3.

Bleaching agents other than oxygen bleaching agents are also known in

25 the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in

30 the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.

Builder system

The laundry detergent compositions of the present invention will preferably comprise builder, more preferably an inorganic builder, most preferably Zeolite A and/or Sodium tripolyphosphate. It has been surprisingly found that the laundry detergent composition of the present invention further comprising a builder, provide enhanced food stain/soil removal, dingy cleaning and whiteness maintenance. Without wishing to be bound by theory, it is believed that the saccharide gums may entrap calcium and thereby limit the enzyme hydrolysis. Therefore, the use of builder is expected to remove the entrapped calcium and favouring the action of the saccharide gums degrading enzyme.

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates, alkyl- or alkenyl-succinic acid and fatty acids, materials such as ethylenediamine tetraacetate, diethylene triamine pentamethyleneacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B, HS or MAP.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$).

Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-

soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydro-furan - cis, cis, cis-tetracarboxylates, 2,5-tetrahydro-furan -cis -dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic poly-carboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Preferred builder systems for use in the present compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid. Other preferred builder systems include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid. Preferred builder systems for use in liquid detergent compositions of the present invention are soaps and polycarboxylates.

Other builder materials that can form part of the builder system for use in granular compositions include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

5 Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with
10 maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 5% to 80% by weight of the composition preferably from 10% to 70% and most
15 usually from 30% to 60% by weight.

Other surfactant system

The laundry detergent compositions of the present invention may also
20 contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

Ampholytic surfactants are also suitable for use in the laundry detergent
25 compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18
30 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

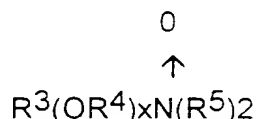
When included therein, the laundry detergent compositions of the present
35 invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

Zwitterionic surfactants are also suitable for use in laundry detergent compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula :



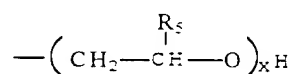
wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C₁₀-C₁₈ alkyl dimethyl amine oxides and C₈-C₁₂ alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

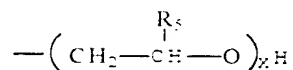
The laundry detergent composition of the present invention may further comprise a cosurfactant selected from the group of primary or tertiary amines. Suitable primary amines for use herein include amines according to the formula R₁NH₂ wherein R₁ is a C₆-C₁₂, preferably C₆-C₁₀ alkyl chain or R₄X(CH₂)_n, X is -O-, -C(O)NH- or -NH-, R₄ is a C₆-C₁₂ alkyl chain n is between 1 to 5, preferably 3. R₁ alkyl chains may be straight or branched and may be interrupted with up to 12, preferably less than 5 ethylene oxide moieties. Preferred amines according to the formula herein above are n-alkyl amines. Suitable amines for use herein may be selected from 1-hexylamine, 1-octylamine, 1-decylamine and laurylamine. Other preferred primary amines include C₈-C₁₀ oxypropylamine, octyloxypropylamine, 2-ethylhexyloxypropylamine, lauryl amido propylamine and amido propylamine.

Suitable tertiary amines for use herein include tertiary amines having the formula R₁R₂R₃N wherein R₁ and R₂ are C₁-C₈ alkylchains or



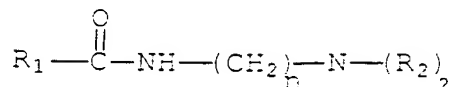
R₃ is either a C₆-C₁₂, preferably C₆-C₁₀ alkyl chain, or R₃ is R₄X(CH₂)_n, whereby X is -O-, -C(O)NH- or -NH-, R₄ is a C₄-C₁₂, n is between 1 to 5, preferably 2-3. R₅ is H or C₁-C₂ alkyl and x is between 1 to 6. R₃ and R₄ may be linear or branched; R₃ alkyl chains may be interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

Preferred tertiary amines are R₁R₂R₃N where R₁ is a C₆-C₁₂ alkyl chain, R₂ and R₃ are C₁-C₃ alkyl or



where R₅ is H or CH₃ and x = 1-2.

Also preferred are the amidoamines of the formula:



- 5 wherein R_1 is C_6 - C_{12} alkyl; n is 2-4,
preferably n is 3; R_2 and R_3 is C_1 - C_4

Most preferred amines of the present invention include 1-octylamine, 1-hexylamine, 1-decylamine, 1-dodecylamine, C8-10oxypropylamine, N coco 1-
10 3diaminopropane, coconutalkyldimethylamine, lauryldimethylamine, lauryl bis(hydroxyethyl)amine, coco bis(hydroxyethyl)amine, lauryl amine 2 moles propoxylated, octyl amine 2 moles propoxylated, lauryl amidopropyldimethylamine, C8-10 amidopropyldimethylamine and C10 amidopropyldimethylamine.

15 The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecyldimethylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

20

Colour care and fabric care benefits

Technologies which provide a type of colour care benefit can also be included. Examples of these technologies are metallo catalysts for colour
25 maintenance. Such metallo catalysts are described in copending European Patent Application No. 92870181.2. Dye fixing agents, polyolefin dispersion for anti-wrinkles and improved water absorbancy, perfume and amino-functional polymer for color care treatment and perfume substantivity are further examples of color care / fabric care technologies and are described in the co-
30 pending Patent Application No. 96870140.9, filed November 07, 1996.

Fabric softening agents can also be incorporated into laundry detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the
35 smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic

5 fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0 299 575 and 0 313 146.

10 Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide
15 materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

20

Chelating Agents

The laundry detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents
25 can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions
30 by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilo-triacetates, ethylenediamine tetrapropionates, triethylenetetraamine-hexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali
35 metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Suds suppressor

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil®.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

Others

Other components used in laundry detergent compositions may be employed, such as soil-suspending agents, soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and/or encapsulated or non-encapsulated perfumes.

Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB 1,464,616. Other suitable water soluble encapsulating materials comprise dextrans derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrans are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating material consists of a modified maize starch and glucose.

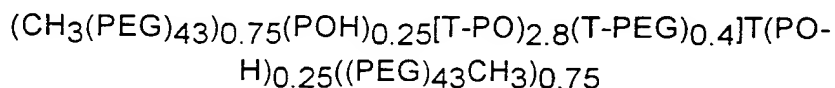
The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

Antiredeposition and soil suspension agents suitable herein include
 5 cellulose derivatives such as methylcellulose, carboxymethylcellulose and
 hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their
 salts. Polymers of this type include the polyacrylates and maleic anhydride-
 acrylic acid copolymers previously mentioned as builders, as well as
 10 copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic
 acid, the maleic anhydride constituting at least 20 mole percent of the
 copolymer. These materials are normally used at levels of from 0.5% to 10%
 by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6%
 by weight of the composition.

15 Preferred optical brighteners are anionic in character, examples of which
 are disodium 4,4'-bis-(2-diethanolamino-4-anilino-s-triazin-6-ylamino)stilbene-
 2:2' disulphonate, disodium 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-
 ylamino)stilbene-2:2' - disulphonate, disodium 4,4' - bis-(2,4-dianilino-s-triazin-
 6-ylamino)stilbene-2:2' - disulphonate, monosodium 4,4' -bis-(2,4-dianilino-s-
 20 tri-azin-6 ylamino)stilbene-2-sulphonate, disodium 4,4' -bis-(2-anilino-4-(N-
 methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2' - disulphonate,
 di-sodium 4,4' -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2' disulphonate, di-
 so-dium 4,4'bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6- yлами-
 25 no)stilbene-2,2'disulphonate, sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3 -
 triazole-2''-sulphonate and 4,4'-bis(2-sulphostyryl)biphenyl. Highly preferred
 brighteners are the specific brighteners of copending European Patent
 application No. 95201943.8.

Other useful polymeric materials are the polyethylene glycols,
 30 particularly those of molecular weight 1000-10000, more particularly 2000 to
 8000 and most preferably about 4000. These are used at levels of from 0.20%
 to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the
 previously mentioned homo- or co-polymeric polycarboxylate salts are valuable
 for improving whiteness maintenance, fabric ash deposition, and cleaning
 35 performance on clay, proteinaceous and oxidizable soils in the presence of
 transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula :



where PEG is $-(\text{OC}_2\text{H}_4)_n\text{O}-$, PO is $(\text{OC}_3\text{H}_6\text{O})$ and T is $(\text{pCOC}_6\text{H}_4\text{CO})$.

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfobenzoic acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

It is well known in the art that free chlorine in tap water rapidly deactivates the enzymes comprised in detergent compositions. Therefore, using chlorine scavenger such as perborate, ammonium sulfate, sodium sulphite or polyethyleneimine at a level above 0.1% by weight of total composition, in the formulas will provide improved through the wash stability of the detergent enzymes. Compositions comprising chlorine scavenger are

described in the European patent application 92870018.6 filed January 31, 1992.

Alkoxylated polycarboxylates such as those prepared from polyacrylates
5 are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and
10 n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

15

Dispersants

The laundry detergent composition of the present invention can also contain dispersants : Suitable water-soluble organic salts are the homo- or co-
20 polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight
25 of from 1,000 to 100,000.

Especially, copolymer of acrylate and methylacrylate such as the 480N having a molecular weight of 4000, at a level from 0.5-20% by weight of composition can be added in the laundry detergent compositions of the present invention.

30

The compositions of the invention may contain a lime soap peptiser compound, which has preferably a lime soap dispersing power (LSDP), as defined hereinafter of no more than 8, preferably no more than 7, most preferably no more than 6. The lime soap peptiser compound is preferably
35 present at a level from 0% to 20% by weight.

A numerical measure of the effectiveness of a lime soap peptiser is given by the lime soap dispersant power (LSDP) which is determined using the lime soap dispersant test as described in an article by H.C. Borghetty and C.A. Bergman, J. Am. Oil. Chem. Soc., volume 27, pages 88-90, (1950). This lime soap dispersion test method is widely used by practitioners in this art field being referred to, for example, in the following review articles; W.N. Linfield, Surfactant science Series, Volume 7, page 3; W.N. Linfield, Tenside surf. det., volume 27, pages 159-163, (1990); and M.K. Nagarajan, W.F. Masler, Cosmetics and Toiletries, volume 104, pages 71-73, (1989). The LSDP is the % weight ratio of dispersing agent to sodium oleate required to disperse the lime soap deposits formed by 0.025g of sodium oleate in 30ml of water of 333ppm CaCO_3 (Ca:Mg=3:2) equivalent hardness.

Surfactants having good lime soap peptiser capability will include certain amine oxides, betaines, sulfobetaines, alkyl ethoxysulfates and ethoxylated alcohols.

Exemplary surfactants having a LSDP of no more than 8 for use in accord with the present invention include C_{16} - C_{18} dimethyl amine oxide, C_{12} - C_{18} alkyl ethoxysulfates with an average degree of ethoxylation of from 1-5, particularly C_{12} - C_{15} alkyl ethoxysulfate surfactant with a degree of ethoxylation of amount 3 (LSDP=4), and the C_{14} - C_{15} ethoxylated alcohols with an average degree of ethoxylation of either 12 (LSDP=6) or 30, sold under the tradenames Lutensol A012 and Lutensol A030 respectively, by BASF GmbH.

Polymeric lime soap peptisers suitable for use herein are described in the article by M.K. Nagarajan, W.F. Masler, to be found in Cosmetics and Toiletries, volume 104, pages 71-73, (1989).

Hydrophobic bleaches such as 4-[N-octanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-nonanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-decanoyl-6-aminohexanoyl]benzene sulfonate and mixtures thereof, and nonanoyloxy benzene sulfonate together with hydrophilic / hydrophobic bleach formulations can also be used as lime soap peptisers compounds.

Dye transfer inhibition

The laundry detergent compositions of the present invention can also include compounds for inhibiting dye transfer from one fabric to another of
 5 solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

Polymeric dye transfer inhibiting agents

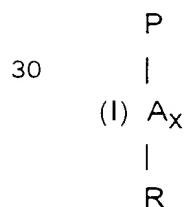
10 The laundry detergent compositions according to the present invention also comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.05% to 1% by weight of polymeric dye transfer inhibiting agents. Said polymeric dye transfer inhibiting agents are normally incorporated into laundry detergent compositions in order to inhibit the transfer of dyes from
 15 colored fabrics onto fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

Especially suitable polymeric dye transfer inhibiting agents are polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole,
 20 polyvinylpyrrolidone polymers, polyvinylloxazolidones and polyvinylimidazoles or mixtures thereof.

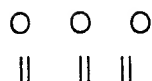
Addition of such polymers also enhances the performance of the enzymes according to the invention.

25 a) Polyamine N-oxide polymers

The polyamine N-oxide polymers suitable for use contain units having the following structure formula :



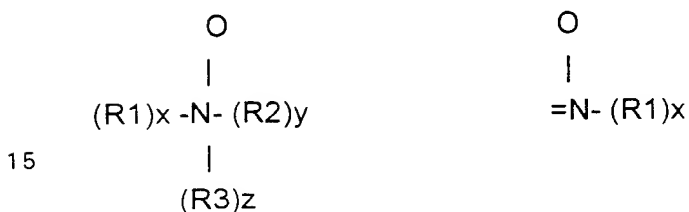
35 wherein P is a polymerisable unit, whereto the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.



A is NC, CO, C, -O-, -S-, -N-; x is 0 or 1;

5 R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

10 The N-O group can be represented by the following general structures :



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1
20 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.
25 Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group.
30 Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

35

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group.

5 Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups.

10 Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, 15 polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by 20 appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other 25 monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a $PK_a < 10$, preferably $PK_a < 7$, more preferred $PK_a < 6$.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the 30 desired water-solubility and dye-suspending power.

Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.



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1

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

The N-vinylimidazole N-vinylpyrrolidone polymers used in the present invention have an average molecular weight range from 5,000-1,000,000, preferably from 5,000-200,000.

5 Highly preferred polymers for use in detergent compositions according to the present invention comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000.

10 The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113, "Modern Methods of Polymer Characterization".

Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have an average molecular weight range from 5,000 to 50,000; more preferably from 8,000 to 30,000; most preferably from 10,000 to 20,000.

20 The N-vinylimidazole N-vinylpyrrolidone copolymers characterized by having said average molecular weight range provide excellent dye transfer inhibiting properties while not adversely affecting the cleaning performance of detergent compositions formulated therewith.

The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4 .

25 c) Polyvinylpyrrolidone

 The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12; polyvinylpyrrolidones known to

persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

d) Polyvinylloxazolidone :

5 The detergent compositions of the present invention may also utilize polyvinylloxazolidone as a polymeric dye transfer inhibiting agent. Said polyvinylloxazolidones have an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about
10 5,000 to about 15,000.

e) Polyvinylimidazole :

 The detergent compositions of the present invention may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said
15 polyvinylimidazoles have an average about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

f) Cross-linked polymers :

20 Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups in the backbone or on branches; cross-linked polymers have been described in the Journal of Polymer Science, volume 22, pages 1035-1039. In one embodiment, the cross-linked polymers are made in such a way
25 that they form a three-dimensional rigid structure, which can entrap dyes in the pores formed by the three-dimensional structure. In another embodiment, the cross-linked polymers entrap the dyes by swelling. Such cross-linked polymers are described in the co-pending patent application 94870213.9

30 **Method of washing**

 The compositions of the invention may be used in essentially any washing or cleaning methods, including soaking methods, pretreatment methods and methods with rinsing steps for which a separate rinse aid
35 composition may be added.

The process described herein comprises contacting fabrics with a laundering solution in the usual manner and exemplified hereunder.

The process of the invention is conveniently carried out in the course of the cleaning process. The method of cleaning is preferably carried out at 5°C to 95°C, especially between 10°C and 60°C. The pH of the treatment solution is preferably from 7 to 11.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

In the detergent compositions, the enzymes levels are expressed by pure enzyme by weight of the total composition and unless otherwise specified, the detergent ingredients are expressed by weight of the total compositions. The abbreviated component identifications therein have the following meanings:

LAS	: Sodium linear C ₁₁₋₁₃ alkyl benzene sulphonate.
TAS	: Sodium tallow alkyl sulphate.
CxyAS	: Sodium C _{1x} - C _{1y} alkyl sulfate.
CxySAS	: Sodium C _{1x} - C _{1y} secondary (2,3) alkyl sulfate.
CxyEz	: C _{1x} - C _{1y} predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide.
CxyEzS	: C _{1x} - C _{1y} sodium alkyl sulfate condensed with an average of z moles of ethylene oxide.
QAS	: R ₂ .N+(CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₁₂ -C ₁₄ .
QAS 1	: R ₂ .N+(CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₈ -C ₁₁ .
APA	: C ₈₋₁₀ amido propyl dimethyl amine.
Soap	: Sodium linear alkyl carboxylate derived from a 80/20 mixture of tallow and coconut fatty acids.
Nonionic	: C ₁₃ -C ₁₅ mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5.
Neodol 45-13	: C ₁₄ -C ₁₅ linear primary alcohol ethoxylate, sold by Shell Chemical CO.

Quat	: Quaternary surfactant selected from one or more of the following: lauryl trimethyl ammonium chloride, myristyl trimethyl ammonium chloride, palmityl trimethyl ammonium chloride, coconut trimethylammonium chloride, coconut trimethylammonium methylsulfate, coconut dimethyl-monohydroxyethyl-ammonium chloride, coconut dimethyl-monohydroxyethylammonium methylsulfate, steryl dimethyl-monohydroxy-ethylammonium chloride, steryl dimethylmonohydroxy-ethylammonium methylsulfate, di- C ₁₂ -C ₁₄ alkyl dimethyl ammonium chloride.
STS	: Sodium toluene sulphonate.
CFAA	: C ₁₂ -C ₁₄ alkyl N-methyl glucamide.
TFAA	: C ₁₆ -C ₁₈ alkyl N-methyl glucamide.
TPKFA	: C ₁₂ -C ₁₄ topped whole cut fatty acids.
DEQA	: Di-(tallow-oxy-ethyl) dimethyl ammonium chloride.
DEQA (2)	: Di-(soft-tallowyloxyethyl) hydroxyethyl methyl ammonium methylsulfate.
DTDMAMS	: Ditallow dimethyl ammonium methylsulfate.
SDASA	: 1:2 ratio of stearyldimethyl amine:triple-pressed stearic acid.
Silicate	: Amorphous Sodium Silicate (SiO ₂ :Na ₂ O ratio = 1.6-3.2).
Zeolite A	: Hydrated Sodium Aluminosilicate of formula Na ₁₂ (AlO ₂ SiO ₂) ₁₂ . 27H ₂ O having a primary particle size in the range from 0.1 to 10 micrometers (Weight expressed on an anhydrous basis).
Na-SKS-6	: Crystalline layered silicate of formula δ -Na ₂ Si ₂ O ₅ .
Citrate	: Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425 and 850 micrometres.
Citric	: Anhydrous citric acid.
Borate	: Sodium borate
Carbonate	: Anhydrous sodium carbonate with a particle size between 200 and 900 micrometres.
Bicarbonate	: Anhydrous sodium hydrogen carbonate with a particle size distribution between 400 and 1200 micrometres.
Sulphate	: Anhydrous sodium sulphate.

Mg Sulphate	: Anhydrous magnesium sulfate.
STPP	: Sodium tripolyphosphate.
TSPP	: Tetrasodium pyrophosphate.
MA/AA	: Random copolymer of 4:1 acrylate/maleate, average molecular weight about 70,000-80,000.
MA/AA 1	: Random copolymer of 6:4 acrylate/maleate, average molecular weight about 10,000.
AA	: Sodium polyacrylate polymer of average molecular weight 4,500.
PB1	: Anhydrous sodium perborate monohydrate of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$.
PB4	: Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$.
Percarbonate	: Anhydrous sodium percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$.
NaDCC	: Sodium dichloroisocyanurate.
TAED	: Tetraacetythylenediamine.
NOBS	: Nonanoyloxybenzene sulfonate in the form of the sodium salt.
NACA-OBS	: (6-nonamidocaproyl) oxybenzene sulfonate.
DTPA	: Diethylene triamine pentaacetic acid.
HEDP	: 1,1-hydroxyethane diphosphonic acid.
DETPMP	: Diethyltriamine penta (methylene) phosphonate, marketed by Monsanto under the Trade name Dequest 2060.
EDDS	: Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt
Photoactivated Bleach	: Sulfonated zinc phthalocyanine encapsulated in dextrin soluble polymer.
Photoactivated Bleach 1	: Sulfonated aluminophthalocyanine encapsulated in dextrin soluble polymer.
PAAC	: Pentaamine acetate cobalt(III) salt.
Mannanase	: Mannanase sold under the tradename Gamanase by Novo Nordisk A/S and/or Galactomannase extracted from the enzyme product sold under the tradename Rohapec B1L by Rohm.

Protease	: Proteolytic enzyme sold under the tradename Savinase, Alcalase, Durazym by Novo Nordisk A/S, Maxacal, Maxapem sold by Gist-Brocades and proteases described in patents WO91/06637 and/or WO95/10591 and/or EP 251 446.
Amylase	: Amylolytic enzyme sold under the tradename Purafact Ox Am ^R described in WO 94/18314, WO96/05295 sold by Genencor; Termamyl [®] , Fungamyl [®] and Duramyl [®] , all available from Novo Nordisk A/S and those described in WO95/26397.
Lipase	: Lipolytic enzyme sold under the tradename Lipolase, Lipolase Ultra by Novo Nordisk A/S and Lipomax by Gist-Brocades.
Cellulase	: Cellulytic enzyme sold under the tradename Carezyme, Celluzyme and/or Endolase by Novo Nordisk A/S.
CMC	: Sodium carboxymethyl cellulose.
PVP	: Polyvinyl polymer, with an average molecular weight of 60,000.
PVNO	: Polyvinylpyridine-N-Oxide, with an average molecular weight of 50,000.
PVPVI	: Copolymer of vinylimidazole and vinylpyrrolidone, with an average molecular weight of 20,000.
Brightener 1	: Disodium 4,4'-bis(2-sulphostyryl)biphenyl.
Brightener 2	: Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl) stilbene-2:2'-disulfonate.
Silicone antifoam	: Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.
Suds Suppressor	: 12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form.
Opacifier	: Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621.
SRP 1	: Anionically end capped poly esters.
SRP 2	: Diethoxylated poly (1,2 propylene terephthalate) short block polymer.

QEA	: bis((C ₂ H ₅ O)(C ₂ H ₄ O) _n)(CH ₃) -N ⁺ -C ₆ H ₁₂ -N ⁺ -(CH ₃) bis((C ₂ H ₅ O)-(C ₂ H ₄ O)) _n , wherein n = from 20 to 30.
PEI	: Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogen.
Polymer A	: Modified polyamines of PEI (MW = 182) with average degree of ethoxylation = 15.
Polymer B	: Modified polyamines of PEI (MW = 600) with average degree of ethoxylation = 20.
Polyamide-polyamine	Polyamide-polyamines herein are commercially marketed under the tradenames: Kymene [®] , Kymene 557H [®] , Kymene 557LX [®] , Reten [®] , and Cartaretin [®] .
SCS	: Sodium cumene sulphonate.
HMWPEO	: High molecular weight polyethylene oxide.
PEG _x	: Polyethylene glycol, of a molecular weight of x .
PEO	: Polyethylene oxide, with an average molecular weight of 5,000.
TEPAE	: Tetraethylenepentaamine ethoxylate.

Example 1

The following high density laundry detergent compositions were prepared according to the present invention :

5

	I	II	III	IV	V	VI
LAS	8.0	8.0	8.0	2.0	6.0	6.0
TAS	-	0.5	-	0.5	1.0	0.1
C46(S)AS	2.0	2.5	-	-	-	-
C25AS	-	-	-	7.0	4.5	5.5
C68AS	2.0	5.0	7.0	-	-	-
C25E5	-	-	3.4	10.0	4.6	4.6
C25E7	3.4	3.4	1.0	-	-	-
C25E3S	-	-	-	2.0	5.0	4.5
QAS	-	0.8	-	-	-	-
QAS 1	-	-	-	0.8	0.5	1.0
Zeolite A	18.1	18.0	14.1	18.1	20.0	18.1
Citric	-	-	-	2.5	-	2.5
Carbonate	13.0	13.0	27.0	10.0	10.0	13.0
Na-SKS-6	-	-	-	10.0	-	10.0
Silicate	1.4	1.4	3.0	0.3	0.5	0.3
Citrate	-	1.0	-	3.0	-	-
Sulfate	26.1	26.1	26.1	6.0	-	-
Mg sulfate	0.3	-	-	0.2	-	0.2
MA/AA	0.3	0.3	0.3	4.0	1.0	1.0
CMC	0.2	0.2	0.2	0.2	0.4	0.4
PB4	9.0	9.0	5.0	-	-	-
Percarbonate	-	-	-	-	18.0	18.0
TAED	1.5	0.4	1.5	-	3.9	4.2
NACA-OBS	-	2.0	1.0	-	-	-
DETPMP	0.25	0.25	0.25	0.25	-	-
SRP 1	-	-	-	0.2	-	0.2
EDDS	-	0.25	0.4	-	0.5	0.5
CFAA	-	1.0	-	2.0	-	-
HEDP	0.3	0.3	0.3	0.3	0.4	0.4
QEA	-	-	-	0.2	-	0.5
Mannanase	0.005	0.002	0.0008	0.001	0.002	0.001

Protease	0.009	0.009	0.01	0.04	0.05	0.03
Amylase	0.002	0.002	0.002	0.006	0.008	0.008
Cellulase	0.0007	-	-	0.0007	0.0007	0.0007
Lipase	0.006	-	-	0.01	0.01	0.01
Photoactivated bleach (ppm)	15	15	15	-	20	20
PVNO/PVPVI	-	-	-	0.1	-	-
Brightener 1	0.09	0.09	0.09	-	0.09	0.09
Perfume	0.3	0.3	0.3	0.4	0.4	0.4
Silicone antifoam	0.5	0.5	0.5	-	0.3	0.3
Density in g/litre	850	850	850	850	850	850
Miscellaneous and minors	Up to 100%					

Example 2

The following granular laundry detergent compositions of particular utility under European machine wash conditions were prepared according to the present invention :

	I	II	III	IV	V	VI
LAS	5.5	7.5	5.0	5.0	6.0	7.0
TAS	1.25	1.9	-	0.8	0.4	0.3
C24AS/C25AS	-	2.2	5.0	5.0	5.0	2.2
C25E3S	-	0.8	1.0	1.5	3.0	1.0
C45E7	3.25	-	-	-	-	3.0
TFAA	-	-	2.0	-	-	-
C25E5	-	5.5	-	-	-	-
QAS	0.8	-	-	-	-	-
QAS 1	-	0.7	1.0	0.5	1.0	0.7
STPP	19.7	-	-	-	-	-
Zeolite A	-	19.5	25.0	19.5	20.0	17.0
NaSKS-6/citric acid (79:21)	-	10.6	-	10.6	-	-
Na-SKS-6	-	-	9.0	-	10.0	10.0
Carbonate	6.1	21.4	9.0	10.0	10.0	18.0
Bicarbonate	-	2.0	7.0	5.0	-	2.0
Silicate	6.8	-	-	0.3	0.5	-
Citrate	-	-	4.0	4.0	-	-
Sulfate	39.8	-	-	5.0	-	12.0
Mg sulfate	-	-	0.1	0.2	0.2	-
MA/AA	0.5	1.6	3.0	4.0	1.0	1.0
CMC	0.2	0.4	1.0	1.0	0.4	0.4
PB4	5.0	12.7	-	-	-	-
Percarbonate	-	-	-	-	18.0	15.0
TAED	0.5	3.1	-	-	5.0	-
NACA-OBS	1.0	3.5	-	-	-	2.5
DETPMP	0.25	0.2	0.3	0.4	-	0.2
HEDP	-	0.3	-	0.3	0.3	0.3
QEA	-	-	1.0	1.0	1.0	-
Mannanase	0.005	0.002	0.008	0.005	0.002	0.001

Protease	0.009	0.03	0.03	0.05	0.05	0.02
Lipase	0.003	0.003	0.006	0.006	0.006	0.004
Cellulase	0.0006	0.0006	0.0005	0.0005	0.0007	0.0007
Amylase	0.002	0.002	0.006	0.006	0.01	0.003
PVNO/PVPVI	-	-	0.2	0.2	-	-
PVP	0.9	1.3	-	-	-	0.9
SRP 1	-	-	0.2	0.2	0.2	-
Photoactivated bleach (ppm)	15	27	-	-	20	20
Photoactivated bleach 1 (ppm)	15	-	-	-	-	-
Brightener 1	0.08	0.2	-	-	0.09	0.15
Brightener 2	-	0.04	-	-	-	-
Perfume	0.3	0.5	0.4	0.3	0.4	0.3
Silicone antifoam	0.5	2.4	0.3	0.5	0.3	2.0
Density in g/litre	750	750	750	750	750	750
Miscellaneous and minors	Up to 100%					

Example 3

The following detergent compositions of particular utility under European machine wash conditions were prepared according to the present invention :

5

	I	II	III	IV
Blown Powder				
LAS	6.0	5.0	11.0	6.0
TAS	2.0	-	-	2.0
Zeolite A	24.0	-	-	20.0
STPP	-	27.0	24.0	-
Sulfate	4.0	6.0	13.0	-
MA/AA	1.0	4.0	6.0	2.0
Silicate	1.0	7.0	3.0	3.0
CMC	1.0	1.0	0.5	0.6
Brightener 1	0.2	0.2	0.2	0.2
Silicone antifoam	1.0	1.0	1.0	0.3
DETPMP	0.4	0.4	0.2	0.4
Spray On				
Brightener	0.02	-	-	0.02
C45E7	-	-	-	5.0
C45E2	2.5	2.5	2.0	-
C45E3	2.6	2.5	2.0	-
Perfume	0.5	0.3	0.5	0.2
Silicone antifoam	0.3	0.3	0.3	-
Dry additives				
QEA	-	-	-	1.0
EDDS	0.3	-	-	-
Sulfate	2.0	3.0	5.0	10.0
Carbonate	6.0	13.0	15.0	14.0
Citric	2.5	-	-	2.0
QAS 1	0.5	-	-	0.5
Na-SKS-6	10.0	-	-	-
Percarbonate	18.5	-	-	-
PB4	-	18.0	10.0	21.5
TAED	2.0	2.0	-	2.0
NACA-OBS	3.0	2.0	4.0	-

Mannanase	0.005	0.002	0.0008	0.001
Protease	0.03	0.03	0.03	0.03
Lipase	0.008	0.008	0.008	0.004
Amylase	0.003	0.003	0.003	0.006
Brightener 1	0.05	-	-	0.05
Miscellaneous and minors		Up to 100%		

Example 4

The following granular detergent compositions were prepared according to the present invention :

5

	I	II	III	IV	V	VI
Blown Powder						
LAS	23.0	8.0	7.0	9.0	7.0	7.0
TAS	-	-	-	-	1.0	-
C45AS	6.0	6.0	5.0	8.0	-	-
C45AES	-	1.0	1.0	1.0	-	-
C45E35	-	-	-	-	2.0	4.0
Zeolite A	10.0	18.0	14.0	12.0	10.0	10.0
MA/AA	-	0.5	-	-	-	2.0
MA/AA 1	7.0	-	-	-	-	-
AA	-	3.0	3.0	2.0	3.0	3.0
Sulfate	5.0	6.3	14.3	11.0	15.0	19.3
Silicate	10.0	1.0	1.0	1.0	1.0	1.0
Carbonate	15.0	20.0	10.0	20.7	8.0	6.0
PEG 4000	0.4	1.5	1.5	1.0	1.0	1.0
DTPA	-	0.9	0.5	-	-	0.5
Brightener 2	0.3	0.2	0.3	-	0.1	0.3
Spray On						
C45E7	-	2.0	-	-	2.0	2.0
C25E9	3.0	-	-	-	-	-
C23E9	-	-	1.5	2.0	-	2.0
Perfume	0.3	0.3	0.3	2.0	0.3	0.3
Agglomerates						
C45AS	-	5.0	5.0	2.0	-	5.0
LAS	-	2.0	2.0	-	-	2.0
Zeolite A	-	7.5	7.5	8.0	-	7.5
Carbonate	-	4.0	4.0	5.0	-	4.0
PEG 4000	-	0.5	0.5	-	-	0.5
Misc (Water etc.)	-	2.0	2.0	2.0	-	2.0
Dry additives						
QAS	-	-	-	-	1.0	-
Citric	-	-	-	-	2.0	-

PB4	-	-	-	-	12.0	1.0
PB1	4.0	1.0	3.0	2.0	-	-
Percarbonate	-	-	-	-	2.0	10.0
Carbonate	-	5.3	1.8	-	4.0	4.0
NOBS	4.0	-	6.0	-	-	0.6
Methyl cellulose	0.2	-	-	-	-	-
Na-SKS-6	8.0	-	-	-	-	-
STS	-	-	2.0	-	1.0	-
Culmene sulfonic acid	-	1.0	-	-	-	2.0
Mannanase	0.005	0.002	0.001	0.008	0.001	0.001
Protease	0.02	0.02	0.02	0.01	0.02	0.02
Lipase	0.004	-	0.004	-	0.004	0.008
Amylase	0.003	-	0.002	-	0.003	-
Cellulase	0.0005	0.0005	0.0005	0.0007	0.0005	0.0005
PVPVI	-	-	-	-	0.5	0.1
PVP	-	-	-	-	0.5	-
PVNO	-	-	0.5	0.3	-	-
QEA	-	-	-	-	1.0	-
SRP 1	0.2	0.5	0.3	-	0.2	-
Silicone antifoam	0.2	0.4	0.2	0.4	0.1	-
Mg sulfate	-	-	0.2	-	0.2	-
Miscellaneous and minors				Up to 100%		

Example 5

The following nil bleach-containing detergent compositions of particular use in the washing of coloured clothing were prepared according to the present invention :

	I	II	III
Blown Powder			
Zeolite A	15.0	15.0	-
Sulfate	-	5.0	-
LAS	3.0	3.0	-
DETPMP	0.4	0.5	-
CMC	0.4	0.4	-
MA/AA	4.0	4.0	-
Agglomerates			
C45AS	-	-	11.0
LAS	6.0	5.0	-
TAS	3.0	2.0	-
Silicate	4.0	4.0	-
Zeolite A	10.0	15.0	13.0
CMC	-	-	0.5
MA/AA	-	-	2.0
Carbonate	9.0	7.0	7.0
Spray-on			
Perfume	0.3	0.3	0.5
C45E7	4.0	4.0	4.0
C25E3	2.0	2.0	2.0
Dry additives			
MA/AA	-	-	3.0
Na-SKS-6	-	-	12.0
Citrate	10.0	-	8.0
Bicarbonate	7.0	3.0	5.0
Carbonate	8.0	5.0	7.0
PVPVI/PVNO	0.5	0.5	0.5
Mannanase	0.0008	0.0005	0.001
Protease	0.03	0.02	0.05
Lipase	0.008	0.008	0.008

Amylase	0.01	0.01	0.01
Cellulase	0.001	0.001	0.001
Silicone antifoam	5.0	5.0	5.0
Sulfate	-	9.0	-
Density (g/litre)	700	700	700
Miscellaneous and minors		Up to 100%	

Example 6

The following detergent compositions were prepared according to the present invention :

5

	I	II	III	IV
Base granule				
Zeolite A	30.0	22.0	24.0	10.0
Sulfate	10.0	5.0	10.0	7.0
MA/AA	3.0	-	-	-
AA	-	1.6	2.0	-
MA/AA 1	-	12.0	-	6.0
LAS	14.0	10.0	9.0	20.0
C45AS	8.0	7.0	9.0	7.0
C45AES	-	1.0	1.0	-
Silicate	-	1.0	0.5	10.0
Soap	-	2.0	-	-
Brightener 1	0.2	0.2	0.2	0.2
Carbonate	6.0	9.0	10.0	10.0
PEG 4000	-	1.0	1.5	-
DTPA	-	0.4	-	-
Spray On				
C25E9	-	-	-	5.0
C45E7	1.0	1.0	-	-
C23E9	-	1.0	2.5	-
Perfume	0.2	0.3	0.3	-
Dry additives				
Carbonate	5.0	10.0	18.0	8.0
PVPVI/PVNO	0.5	-	0.3	-
Mannanase	0.005	0.002	0.0008	0.001
Protease	0.03	0.03	0.03	0.02
Lipase	0.008	-	-	0.008
Amylase	0.002	-	-	0.002
Cellulase	0.0002	0.0005	0.0005	0.0002
NOBS	-	4.0	-	4.5
PB1	1.0	5.0	1.5	6.0
Sulfate	4.0	5.0	-	5.0

SRP 1	-	0.4	-	-
Suds suppressor	-	0.5	0.5	-
Miscellaneous and minors		Up to 100%		

Example 7

The following granular detergent compositions were prepared according to the present invention :

5

	I	II	III
Blown Powder			
Zeolite A	20.0	-	15.0
STPP	-	20.0	-
Sulfate	-	-	5.0
Carbonate	-	-	5.0
TAS	-	-	1.0
LAS	6.0	6.0	6.0
C68AS	2.0	2.0	-
Silicate	3.0	8.0	-
MA/AA	4.0	2.0	2.0
CMC	0.6	0.6	0.2
Brightener 1	0.2	0.2	0.1
DETPMP	0.4	0.4	0.1
STS	-	-	1.0
Spray On			
C45E7	5.0	5.0	4.0
Silicone antifoam	0.3	0.3	0.1
Perfume	0.2	0.2	0.3
Dry additives			
QEA	-	-	1.0
Carbonate	14.0	9.0	10.0
PB1	1.5	2.0	-
PB4	18.5	13.0	13.0
TAED	2.0	2.0	2.0
QAS	-	-	1.0
Photoactivated bleach	15 ppm	15 ppm	15 ppm
Na-SKS-6	-	-	3.0
Mannanase	0.005	0.002	0.0008
Protease	0.03	0.03	0.007
Lipase	0.004	0.004	0.004
Amylase	0.006	0.006	0.003

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	Cellulase	0.0002	0.0002	0.0005
	Sulfate	10.0	20.0	5.0
Density (g/litre)		700	700	700
Miscellaneous and minors			Up to 100%	

Example 8

The following detergent compositions were prepared according to the present invention :

5

	I	II	III
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sulfate	-	5.0	-
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DETPMP	0.4	0.2	0.4
EDDS	-	0.4	0.2
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerate			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
Dry Additives			
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
TAED	6.0	2.0	5.0
PB1	14.0	7.0	10.0
PEO	-	-	0.2
Bentonite clay	-	-	10.0
Mannanase	0.005	0.002	0.0008
Protease	0.03	0.03	0.03
Lipase	0.008	0.008	0.008

Cellulase	0.001	0.001	0.001
Amylase	0.01	0.01	0.01
Silicone antifoam	5.0	5.0	5.0
Sulfate	-	3.0	-
Density (g/litre)	850	850	850
Miscellaneous and minors		Up to 100%	

Example 9

The following detergent compositions were prepared according to the present invention :

5

	I	II	III	IV
LAS	18.0	14.0	24.0	20.0
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C23E56.5	-	-	1.0	-
C45E7	-	1.0	-	-
C45E3S	1.0	2.5	1.0	-
STPP	32.0	18.0	30.0	22.0
Silicate	9.0	5.0	9.0	8.0
Carbonate	11.0	7.5	10.0	5.0
Bicarbonate	-	7.5	-	-
PB1	3.0	1.0	-	-
PB4	-	1.0	-	-
NOBS	2.0	1.0	-	-
DETPMP	-	1.0	-	-
DTPA	0.5	-	0.2	0.3
SRP 1	0.3	0.2	-	0.1
MA/AA	1.0	1.5	2.0	0.5
CMC	0.8	0.4	0.4	0.2
PEI	-	-	0.4	-
Sulfate	20.0	10.0	20.0	30.0
Mg sulfate	0.2	-	0.4	0.9
Mannanase	0.005	0.002	0.005	0.001
Protease	0.03	0.03	0.02	0.02
Amylase	0.008	0.007	-	0.004
Lipase	0.004	-	0.002	-
Cellulase	0.0003	-	-	0.0001
Photoactivated bleach	30 ppm	20 ppm	-	10 ppm
Perfume	0.3	0.3	0.1	0.2
Brightener 1/2	0.05	0.02	0.08	0.1
Miscellaneous and minors		up to 100%		

Example 10

The following liquid detergent formulations were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

	I	II	III	IV	V
LAS	11.5	8.8	-	3.9	-
C25E2.5S	-	3.0	18.0	-	16.0
C45E2.25S	11.5	3.0	-	15.7	-
C23E9	-	2.7	1.8	2.0	1.0
C23E7	3.2	-	-	-	-
CFAA	-	-	5.2	-	3.1
TPKFA	1.6	-	2.0	0.5	2.0
Citric (50%)	6.5	1.2	2.5	4.4	2.5
Ca formate	0.1	0.06	0.1	-	-
Na formate	0.5	0.06	0.1	0.05	0.05
SCS	4.0	1.0	3.0	1.2	-
Borate	0.6	-	3.0	2.0	2.9
Na hydroxide	5.8	2.0	3.5	3.7	2.7
Ethanol	1.75	1.0	3.6	4.2	2.9
1,2 Propanediol	3.3	2.0	8.0	7.9	5.3
Monoethanolamine	3.0	1.5	1.3	2.5	0.8
TEPAE	1.6	-	1.3	1.2	1.2
Mannanase	0.005	0.001	0.002	0.0005	0.0002
Protease	0.03	0.01	0.03	0.02	0.02
Lipase	-	-	0.002	-	-
Amylase	-	-	-	0.002	-
Cellulase	-	-	0.0002	0.0005	0.0001
SRP 1	0.2	-	0.1	-	-
DTPA	-	-	0.3	-	-
PVNO	-	-	0.3	-	0.2
Brightener 1	0.2	0.07	0.1	-	-
Silicone antifoam	0.04	0.02	0.1	0.1	0.1
Miscellaneous and water					

Example 11

The following liquid detergent formulations were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

	I	II	III	IV
LAS	10.0	13.0	9.0	-
C25AS	4.0	1.0	2.0	10.0
C25E3S	1.0	-	-	3.0
C25E7	6.0	8.0	13.0	2.5
TFAA	-	-	-	4.5
APA	-	1.4	-	-
TPKFA	2.0	-	13.0	7.0
Citric	2.0	3.0	1.0	1.5
Dodeceny / tetradeceny succinic acid	12.0	10.0	-	-
Rapeseed fatty acid	4.0	2.0	1.0	-
Ethanol	4.0	4.0	7.0	2.0
1,2 Propanediol	4.0	4.0	2.0	7.0
Monoethanolamine	-	-	-	5.0
Triethanolamine	-	-	8.0	-
TEPAE	0.5	-	0.5	0.2
DETPMP	1.0	1.0	0.5	1.0
Mannanase	0.0002	0.0005	0.005	0.0005
Protease	0.02	0.02	0.01	0.008
Lipase	-	0.002	-	0.002
Amylase	0.004	0.004	0.01	0.008
Cellulase	-	-	-	0.002
SRP 2	0.3	-	0.3	0.1
Boric acid	0.1	0.2	1.0	2.0
Ca chloride	-	0.02	-	0.01
Brightener 1	-	0.4	-	-
Suds suppressor	0.1	0.3	-	0.1
Opacifier	0.5	0.4	-	0.3
NaOH up to pH	8.0	8.0	7.6	7.7
Miscellaneous and water				

Example 12

The following liquid detergent compositions were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

5

	I	II	III	IV
LAS	25.0	-	-	-
C25AS	-	13.0	18.0	15.0
C25E3S	-	2.0	2.0	4.0
C25E7	-	-	4.0	4.0
TFAA	-	6.0	8.0	8.0
APA	3.0	1.0	2.0	-
TPKFA	-	15.0	11.0	11.0
Citric	1.0	1.0	1.0	1.0
Dodecenyl / tetradecenyl succinic acid	15.0	-	-	-
Rapeseed fatty acid	1.0	-	3.5	-
Ethanol	7.0	2.0	3.0	2.0
1,2 Propanediol	6.0	8.0	10.0	13.0
Monoethanolamine	-	-	9.0	9.0
TEPAE	-	-	0.4	0.3
DETPMP	2.0	1.2	1.0	-
Mannanase	0.0001	0.0002	0.005	0.0005
Protease	0.08	0.02	0.01	0.02
Lipase	-	-	0.003	0.003
Amylase	0.004	0.01	0.01	0.01
Cellulase	-	-	0.004	0.003
SRP 2	-	-	0.2	0.1
Boric acid	1.0	1.5	2.5	2.5
Bentonite clay	4.0	4.0	-	-
Brightener 1	0.1	0.2	0.3	-
Suds suppressor	0.4	-	-	-
Opacifier	0.8	0.7	-	-
NaOH up to pH	8.0	7.5	8.0	8.2
Miscellaneous and water				

Example 13

The following liquid detergent compositions were prepared according to the present invention (Levels are given in parts by weight, enzyme are expressed in pure enzyme) :

	I	II
LAS	27.6	18.9
C45AS	13.8	5.9
C13E8	3.0	3.1
Oleic acid	3.4	2.5
Citric	5.4	5.4
Na hydroxide	0.4	3.6
Ca Formate	0.2	0.1
Na Formate	-	0.5
Ethanol	7.0	-
Monoethanolamine	16.5	8.0
1,2 propanediol	5.9	5.5
Xylene sulfonic acid	-	2.4
TEPAE	1.5	0.8
Protease	0.05	0.02
Mannanase	0.005	0.0002
PEG	-	0.7
Brightener 2	0.4	0.1
Perfume	0.5	0.3
Water and Minors		

Example 14 :

The following gel detergent compositions were prepared according to the present invention :

	I	II	III	IV
C12-15E2.5S	21	20.2	22.7	13.6
C12LAS	-	-	-	9.1
C12-14 glucosamide	4.0	2.5	-	-
C12-14EO7	4.5	-	-	-
C12-15EO9	-	0.6	0.6	0.6
C8-10 amidopropylamine	1.3	-	-	-
C10 amidopropylamine	-	1.3	1.3	1.3
Citric	1.0	5.0	1.0	1.0
C12/14 fatty acid	-	10.0	10.0	10.0
Palm kernal fatty acid	8.0	-	-	-
Rapeseed fatty acid	8.0	-	-	-
Mannase	0.0001	0.0002	0.005	0.0005
Protease	0.02	0.03	0.03	0.03
Lipase	0.001	0.002	0.003	0.002
Amylase	0.003	0.002	0.002	0.002
Cellulase	0.0007	0.0001	0.0001	0.0001
Brightener 1	0.15	0.15	0.15	0.15
Polymer A	0.7	0.6	0.6	0.6
Polymer B	-	1.2	1.2	1.2
Polyamine-polyamide	2.0	1.0	1.0	-
Polyethoxylated-Polyamines	-	2.0	-	-
Soil release agent	-	0.1	0.1	0.1
Ethanol	0.7	0.5	0.5	0.5
1,2-propanediol	4.0	4.0	4.0	4.0
MonoEthanolAmine	0.7	0.5	0.5	0.5
NaOH	2.8	7.0	7.0	7.0
Boric acid	2.0	-	-	-
Borax	-	2.5	2.5	2.5
Suds supressor	-	0.1	0.1	0.1
Polydimethyl siloxane	0.2	-	-	-
Perfume	0.5	0.75	0.75	0.75
Dye	-	0.04	0.04	0.04
Miscellaneous and water		Up to 100%		

Example 15 :

The following gel detergent compositions were prepared according to the present invention :

5

	I	II	III	IV
C12-15E2.5S	18.2	22.6	27.6	22.6
C12-15EO9	0.6	0.6	0.6	0.6
C10 amidopropylamine	1.3	1.3	1.3	1.3
Citric	1.0	1.0	1.0	1.0
C12/14 fatty acid	10.0	10.0	7.5	10.0
Quat	1.0	5.0	-	-
Mannase	0.005	0.001	0.002	0.0005
Protease	0.03	0.01	0.03	0.03
Lipase	0.002	0.002	0.002	0.002
Amylase	0.003	0.002	0.001	0.002
Cellulase	0.0001	0.0004	0.0001	0.0001
Brightener 1	0.15	0.15	0.15	0.15
Polymer A	0.6	0.3	0.6	0.6
Polymer B	1.2	0.6	1.2	1.2
Soil release agent	0.1	0.1	0.1	0.1
Ethanol	0.5	0.5	0.5	0.5
1,2-propanediol	4.0	4.0	4.0	4.0
MonoEthanolAmine	0.5	0.5	0.5	0.5
NaOH	7.0	7.0	7.0	7.0
Boric acid	-	-	-	-
Borax	2.5	2.5	2.5	-
Suds supressor	0.1	0.1	0.1	0.1
Perfume	0.75	0.75	0.75	0.75
Dye	0.04	0.04	0.04	0.04
Miscellaneous and water			Up to 100%	

Example 16

The following granular fabric detergent compositions which provide "softening through the wash" capability were prepared according to the present invention :

5

	I	II
C45AS	-	10.0
LAS	7.6	-
C68AS	1.3	-
C45E7	4.0	-
C25E3	-	5.0
Coco-alkyl-dimethyl hydroxy-ethyl ammonium chloride	1.4	1.0
Citrate	5.0	3.0
Na-SKS-6	-	11.0
Zeolite A	15.0	15.0
MA/AA	4.0	4.0
DETPMP	0.4	0.4
PB1	15.0	-
Percarbonate	-	15.0
TAED	5.0	5.0
Smectite clay	10.0	10.0
HMWPEO	-	0.1
Mannanase	0.01	0.001
Protease	0.02	0.01
Lipase	0.02	0.01
Amylase	0.03	0.005
Cellulase	0.001	-
Silicate	3.0	5.0
Carbonate	10.0	10.0
Suds suppressor	1.0	4.0
CMC	0.2	0.1
Miscellaneous and water	Up to 100%	

Example 17

The following rinse added fabric softener composition was prepared according to the present invention :

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DEQA (2)	20.0
Mannanase	0.0008
Cellulase	0.001
HCL	0.03
Antifoam agent	0.01
Blue dye	25ppm
CaCl ₂	0.20
Perfume	0.90
Miscellaneous and water	Up to 100%

Example 18

The following fabric softener and dryer added fabric conditioner compositions were prepared according to the present invention :

5

	I	II	III	IV	V
DEQA	2.6	19.0	-	-	-
DEQA(2)	-	-	-	-	51.8
DTMAMS	-	-	-	26.0	-
SDASA	-	-	70.0	42.0	40.2
Stearic acid of IV=0	0.3	-	-	-	-
Neodol 45-13	-	-	13.0	-	-
Hydrochloride acid	0.02	0.02	-	-	-
Ethanol	-	-	1.0	-	-
Mannanase	0.0008	0.0002	0.0005	0.005	0.0002
Perfume	1.0	1.0	0.75	1.0	1.5
Glycoperse S-20	-	-	-	-	15.4
Glycerol monostearate	-	-	-	26.0	-
Digeranyl Succinate	-	-	0.38	-	-
Silicone antifoam	0.01	0.01	-	-	-
Electrolyte	-	0.1	-	-	-
Clay	-	-	-	3.0	-
Dye	10ppm	25ppm	0.01	-	-
Water and minors	100%	100%	-	-	-

Example 19

The following laundry bar detergent compositions were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

	I	II	III	VI	V	III	VI	V
LAS	-	-	19.0	15.0	21.0	6.75	8.8	-
C28AS	30.0	13.5	-	-	-	15.75	11.2	22.5
Na Laurate	2.5	9.0	-	-	-	-	-	-
Zeolite A	2.0	1.25	-	-	-	1.25	1.25	1.25
Carbonate	20.0	3.0	13.0	8.0	10.0	15.0	15.0	10.0
Ca Carbonate	27.5	39.0	35.0	-	-	40.0	-	40.0
Sulfate	5.0	5.0	3.0	5.0	3.0	-	-	5.0
TSP	5.0	-	-	-	-	5.0	2.5	-
STPP	5.0	15.0	10.0	-	-	7.0	8.0	10.0
Bentonite clay	-	10.0	-	-	5.0	-	-	-
DETPMP	-	0.7	0.6	-	0.6	0.7	0.7	0.7
CMC	-	1.0	1.0	1.0	1.0	-	-	1.0
Talc	-	-	10.0	15.0	10.0	-	-	-
Silicate	-	-	4.0	5.0	3.0	-	-	-
PVNO	0.02	0.03	-	0.01	-	0.02	-	-
MA/AA	0.4	1.0	-	-	0.2	0.4	0.5	0.4
SRP 1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Mannanase	.0005	.0005	.0008	.0005	.0002	.0002	0.001	.0005
Amylase	-	-	0.01	-	-	-	0.002	-
Protease	-	0.004	-	0.003	0.003	-	-	0.003
Lipase	-	0.002	-	0.002	-	-	-	-
Cellulase	-	.0003	-	-	.0003	.0002	-	-
PEO	-	0.2	-	0.2	0.3	-	-	0.3
Perfume	1.0	0.5	0.3	0.2	0.4	-	-	0.4
Mg sulfate	-	-	3.0	3.0	3.0	-	-	-
Brightener	0.15	0.1	0.15	-	-	-	-	0.1
Photoactivated bleach (ppm)	-	15.0	15.0	15.0	15.0	-	-	15.0

Example 20

The following detergent additive compositions were prepared according to the present invention :

5

	I	II	III
LAS	-	5.0	5.0
STPP	30.0	-	20.0
Zeolite A	-	35.0	20.0
PB1	20.0	15.0	-
TAED	10.0	8.0	-
Mannanase	0.005	0.0002	0.001
Protease	-	0.3	0.3
Amylase	-	0.06	0.06
Minors, water and miscellaneous		Up to 100%	

CLAIMS

1. A laundry detergent composition comprising a saccharide gum degrading enzyme, said enzyme degrading non starch, non cellulose food polysaccharides having a viscosity higher than 800 cps at 1% solution.
2. A laundry detergent composition according to claim 1 wherein said polysaccharide is selected from agar, algin, karawa, tragacanth, guar gum, locus beam, xathan and/or mixtures thereof.
3. A laundry detergent composition according to claims 1-2 wherein the saccharide gum degrading enzyme is selected from Mannosidase, especially β -mannosidase, endo 1,4- β -D mannosidase, endo 1,2- β -D mannosidase; Galactosidase, especially exo 1,3- β -D mannosidase; exo 1,6- β -D-galactosidase and 1,3- β -D-galactosidase; Glucuronidase, glucuronosidase, exo 1,2 or 1,4 glucuronidase; Arabinase, especially endo α -1,5-arabinosidase, exo Arabanase, exo A (α -1,2; α -1,3) arabinofuranosidase, exo B (α -1,3; α -1,5) arabinofuranosidase; Xanthan lyase; Poly(α -L guluronate) lyase; Agarase, Carrageenase and/or mixtures thereof.
4. A laundry detergent composition according to claims 1-3 wherein said saccharide gum degrading enzyme is present at a level of from 0.0001% to 2%, preferably from 0.0005% to 0.1%, more preferably from 0.0006% to 0.015% pure enzyme by weight of total composition.
5. A laundry detergent composition according to claims 1-4 further comprising a surfactant selected from a nonionic, an anionic surfactant, a cationic surfactant and/or mixtures thereof.
6. A laundry detergent composition according to any of the preceding claims further comprising another enzyme, preferably a cellulase and/or amylase.
7. A laundry detergent composition according to any of the preceding claims further comprising a builder, preferably an inorganic builder, more

preferably a builder selected from zeolite A, sodium tripolyphosphate and/or mixtures thereof.

8. A laundry detergent composition according to any of the preceding claims further comprising an activated bleach system.
9. A laundry detergent composition according to any of the preceding claims wherein said a saccharide gum degrading enzyme is alkaline.
10. A laundry detergent composition according to any of the preceding claims characterised in that said composition is in the liquid, paste, gel, bar, tablets, spray, foam, powder or granular form.
11. A laundry gel detergent composition according to claim 10 which comprises from 15% to 40% by weight of an anionic surfactant component which comprises :
 - (i) from 5% to 25% by weight of alkyl polyethoxylate sulfates wherein the alkyl group contains from 10 to 22 carbon atoms and the polyethoxylate chain contains from 0.5 to 15, preferably from 0.5 to 5, more preferably from 0.5 to 4, ethylene oxide moieties; and
 - (ii) from 5% to 20% by weight of fatty acids.
12. A detergent additive comprising a saccharide gum degrading enzyme.
13. A fabric softening composition comprising a saccharide gum degrading enzyme, said enzyme degrading non starch, non cellulose food polysaccharides having a viscosity higher than 800 cps at 1%, and a cationic surfactant comprising two long chain lengths.
14. Use of a saccharide gum degrading enzyme, said enzyme degrading non starch, non cellulose food polysaccharides having a viscosity higher than 800 cps at 1% solution, in a laundry detergent composition, for fabric cleaning and/or fabric stain removal and/or fabric whiteness maintenance and/or fabric softening and/or fabric colour appearance and/or fabric dye transfer inhibition.

15. Use of a saccharide gum degrading enzyme according to claim 14 for the removal of non starch, non cellulose food polysaccharides having a viscosity higher than 800 cps at 1% solution.
16. Use of a saccharide gum degrading enzyme according to claims 14-15 wherein said polysaccharide is selected from agar, algin, karawa, tragacanth, guar gum, locus beam, xathan and/or mixtures thereof.
17. Use of a saccharide gum degrading according to claims 14-16 and a cellulase for the removal of non starch food polysaccharides having a viscosity higher than 800 cps at 1% solution.

Abstract

The present invention relates to laundry detergent compositions, comprising a saccharide gum degrading enzyme providing excellent cleaning performance, especially food stain/soil removal, dingy cleaning and whiteness benefits.

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